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RESEARCH ARTICLE

Structural characterization of sulphate borophosphate glasses containing calcium oxide

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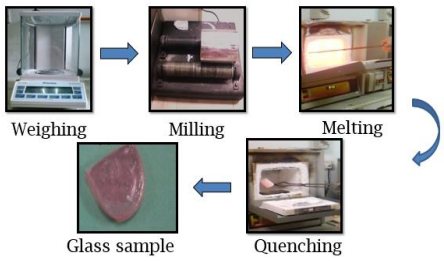
Graphical abstract



Abstract

Increasing demands for better perfoming glasses have lead to current investigating of the sturctural properties of glasses for optimum performances. Calcium sulphate borophosphate glasses of different compositions were prepared using melt quenching technique. The glass forming ability and stability were checked using Differential thermal analyzer (DTA). Density and molar volume had been evaluated and analyzed. From the results of XRD, the absent of discrete and continuous sharp peaks confirmed the amorphous nature of the glass compositions while the results from both IR and Raman revealed the existence of SO_4, BO_4, BO_3, P-O-P and PO_4^{3-}. Addition of $CaSO_4$ to borophosphate influenced the conversion of the dominant BO_3 groups to BO_4 groups. The structure of the samples was mainly based on metaphosphate, diphosphate and BO_4 units, which became depolymerized with addition of $CaSO_4$ content. The glass forming ability and thermal stability were found to increase with an increase in the concentration of modifier content. Glass density and molar volume is found to be between 2.146 to 2.314 gcm^{-3} and 45.794 to 48.880 m^3mol^{-1} respectively. It is observed that the density of glass increased while the molar volume also increased with respect to increase in concentration of $CaSO_4$ in the glass compositions. We analysed our data using different mechanisms and compared the results with previous works. Our findings show that this glass could be beneficial and considered as a good candidate for optical devices applications.

Keywords: Sulphate borophosphate glass, x-ray diffraction, differential thermal analyser, infrared and raman spectroscopy

INTRODUCTION

Borophosphate based glasses have remained the focus of numerous studies due to their unique features for diversity of applications (Karabulut et al., 2015). Glasses containing B_2O_3 are of predominant used as non-linear photonic materials and as laser hosts having high optical parameters (Srinivasulu et al., 2013) . However, unlike silicate and phosphate - based glasses, little studies have been done on borophosphate-glasses.The structural studies of borophosphate network are inspired by way of the enhancement of the glass properties. The role performed with the aid of P_2O_5 and B_2O_3 within the glass structure, and the interplay with other factors within the glass network is a motivating subject of glass technology (Pang et al., 2014). These changes in the network structure of borophosphate glasses can be sensitively detected from the changes in Raman spectra of the borophosphate glasses (Vosejpková et al., 2012). Subsequently, the mixture of the two network formers, B_2O_3 and P_2O_5 allows substantial modifications of the structural and optical properties of the materials compare to simple phosphate and borate host alone (Pang et al., 2014).For instance, the chemical durability can be increased or volume nucleation can be controlled by mixing the phosphate and borate groups. The replacement of alkali oxide with alkaline earth oxide enhances the strength of cross-linking in the glass structure (Edathazhe and Shashikala, 2016). In these glasses the basic units of pure borate glasses are trigonal BO_3 groups, whereas those of pure phosphate glasses are PO_4 tetrahedra linked through covalent bridging oxygen's. The addition of a modifier in some concentration ranges increases the degree of polymerization, the boron coordination changes from trigonal (BO_3) to tetrahedral (BO_4), whereas in phosphate network, an ultra-phosphate network consisting of Q^2 and Q^3 tetrahedral (Kumar et al., 2012a).

In this present study sulphate borophosphate glasses contains calcium oxide was analyzed by melt quenching technique and the structural features of the glasses were determined using X-ray diffraction, Thermal differential analyzer, Fourier transformed infrared and Raman spectroscopy.

EXPERIMENTAL

Materials

The raw materials used for this study were $CaSO_4$ (99.9 % purity), B_2O_3 (99.9% purity) and P_2O_5 (99.9% purity). Glasses in the $xCaSO_4$ - $30B_2O_3$ - (70-x) P_2O_5 with $15 \leq x \leq 35$ mol % system was prepared by melt quenching technique. The homogenized samples mixture was

poured into alumina crucible. The samples were pre-heated in an electric furnace at 300 ^{O}C for 30 minutes and then further heated at 1300 ^{O}C for 1h. The melts glass samples were poured onto a brass plate and annealed at 400 ^{O}C for about 3hours to remove any internal stresses. Then, samples were allowed to cooled to room temperature. Amorphous nature of the glasses was investigated using a Bruker D8 advance diffractometer with Cu – Kα radiations (λ = 1.54Ă) operated at 40kv and 100mA. The powder diffraction patterns were recorded on sample in the range of 2θ = 10°-100° at scanning rate of 0.05°/s.

The density (ρ) of each sample with an error of ± 0.001 gcm^{-3} was measured using Archimedes principle (Analytical balance of specific density-PrecisaXT220A) with toluene (ρ_x = 0.866 gcm^{-3}) as the immersion liquid. The density of each sample is determined by the relation $\rho = \frac{W_a}{W_a - W_b}\rho_x$ where W_a and W_b are the sample weight in air and toluene respectively. The molar volume V_m is calculated from the relation $V_m = \frac{M_{av}}{\rho}$

Thermal properties of the glasses were checked using differential thermal analyzer of Perkin Elmer DTA-7 model. A sample of 11mg in powder form was heated at 10° c/min. The machine operated under a dry nitrogen atmosphere with flow rate of about 200 ml/min. The Hruby parameter H is used to estimate the stability of the prepared glasses from the relation $H_g = \frac{T_c - T_g}{T_m - T_c}$

Fourier transform infrared transmissions spectra were recorded in the spectral range of 400 to 3500 cm^{-1} with Perkin Elmer FTIR 1660 spectrometer. Transparent pellets of each sample were formed by mixing a relatively fine glass powder with KBr at ratio 1:100.

Raman spectrum was obtained using a confocal Horbia Jobin Yvon (Model HR800 UV) in the range of 400 – 1500 cm^{-1}. Argon ion laser was used as radiation source with excitation wavelength of 514.55 nm and power of 5 mW.

RESULTS AND DISCUSSION

X- Ray Diffraction

Fig. 1 shows the X-ray diffraction patterns of the prepared borophosphate glasses recorded in the range of 10° to 100°. The results obtained showed that the X-ray diffraction patterns of the sample exhibited broad diffusion at lower scattering angles around 15-25 degree. It indicated the presence of long range structural disorder and absence of any sharp peak. This result confirms that the prepared samples are completely amorphous.

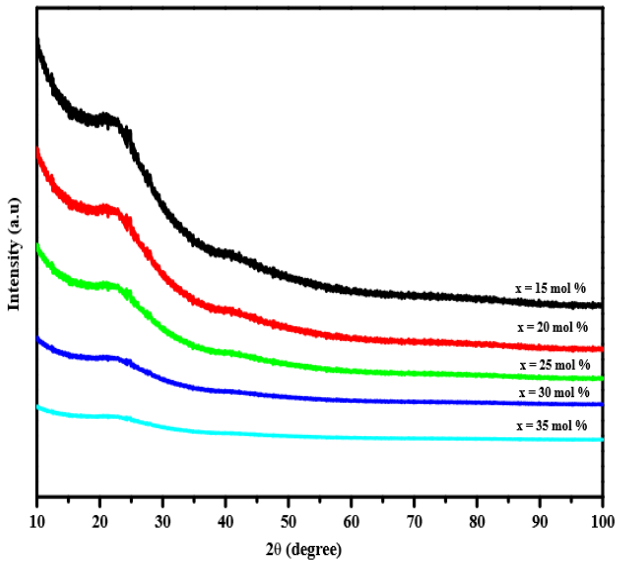


Fig.1 X-ray diffraction of $xCaSO_4$ - $30B_2O_3$ - $(70\text{-}x)P_2O_5$ with 15 ≤ x ≤ 35 mol %.

Density and Molar volume measurements

Fig. 2 depicts the variation of $CaSO_4$ concentration plotted against density and molar volume of borophosphate glasses. The density and molar volume increases with increasing concentration of $CaSO_4$ which indicate an increase of glass network rigidity as shown in Table 1**.** The increase in the glass density is due to an increase in the number of bridging oxygen in the glass (Arunkumar and Marimuthu, 2013). Furthermore, the increase in molar volume results in an increase in inter-atomic spacing or the bond length (Tanko et al., 2016).

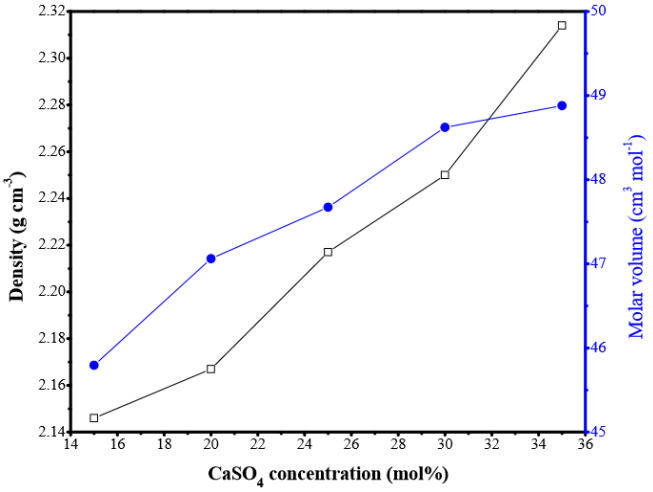


Fig. 2 $CaSO_4$ concentration dependent variation of glass density and molar volume.

Table 1 Norminal composition of $xCaSO_4$ - $30B_2O_3$ - $(70\text{-}x)P_2O_5$ with 15 ≤ x ≤ 35 mol %, density and molar volume of glasses.

Glass code	$xCaSO_4$ mol %	$(70\text{-}x)$ P_2O_5 mol %	30 B_2O_3 mol %	ρ (g cm^{-3}	V_m (cm^3 mol^{-1}
SBP1	15	55	30	2.147	45.794
SBP2	20	50	30	2.167	47.062
SBP3	25	45	30	2.217	47.673
SBP4	30	40	30	2.250	48.622
SBP5	35	35	30	2.314	48.880

Infrared Spectra

The results of the vibrational spectroscopy of IR gives useful structural information about the short and intermediate range in the glass structure (Stefan and Karabulut, 2014, Wan et al., 2014). In general, the main vibrational modes characteristic of atoms in the glass network are observed in the mid- IR region and these modes are independent of the other groups that may be in the glass structure (Ouis et al., 2012). Since the components investigated in this study consist of two main glass formers in different quantities, we expect to detect vibrational modes belonging to both borate and phosphate groups in the IR spectra. The IR spectra of the glasses studied in the range 400 – 3500 cm^{-1} frequency as shown in Fig.3. The strong band observed at 518 to 531 cm^{-1} assigned to bending mode of PO_4^{3-} (Karabulut et al., 2015),the band increased with increasing concentration of $CaSO_4$. Bending of B-O-B linkages of borate network and symmetric bending P-O-P of phosphate is around band at 735-749 cm^{-1} (Saitoh et al., 2015) and band at 850-889 cm^{-1} are assigned to the asymmetric stretching modes of the in-chain P-O-P linkages $(P\text{-}O\text{-}P)_{as}$ (Kumar et al., 2012b). The band at 1049-1071cm^{-1} are a mixture from $\nu(SO_4)$ and $\nu(BO_4)$(Daub et al., 2014) . The bands at 1260-1309 cm^{-1} are assigned to boroxol rings (Rada et al., 2010). The bands around 1429-1443 cm^{-1} have been

assigned to the stretching relaxation of the bond between borate trigonal BO_3 and oxygen units (Leow et al., 2014). Addition of $CaSO_4$ to the glass network can alter the glass lattice, open up the network structure, lower the viscosity, weaken the bond strength of the glass and improve the glass stability (Shen et al.,2015). The variation of the spectra is due to the increase in $CaSO_4$ content. Therefore, this variation creates larger number of non-bridging oxygen in the glass network. As a consequences of that, the phosphate coordination drastically reduces from 4-fold to 3-fold to 2-fold and even dimentional. Therefore, the depolymerization of P-O-P, and B-O-B take place and strength of the glass decreases (Kumar et al., 2012c). However, it was observed that the IR intensities signifies the increase degree of disorder in the network with increase in concentration of $CaSO_4$ .The summary of IR findings and reported values are shown in Table 2.

Raman Spectra

The Raman spectra of $xCaSO_4$ - $30B_2O_5$ - (70-x) P_2O_5 glasses are shown in Fig. 4. The borophosphate glasses reveals one broad vibrational band in the high frequency region with a maximum at 1420 - 1424 cm^{-1} is due to the asymmetric stretching vibration of BO_3 units (Ganguli and Rao, 1999). The band at 1359-1361 cm^{-1} is due to the asymmetric stretching vibration of BO_3 units (Suresh et al., 2012). The band at 1170-1179 cm^{-1} can be ascribed to the symmetric vibration of PO_2 of metaphosphate Q^2 (Kim et al., 2010). The band at 1057 – 1061 cm^{-1} is due to the symmetric stretching vibration of the tetra hedral SO_4 and BO_4 units (Daub et al., 2014). The weak band at 777-780 cm^{-1} can be ascribed to the symmetric strength vibration of BO_3 and BO_4 groups (Vyatchina et al., 2009). The weak band at 615-624 cm^{-1} can be ascribed to the vibrations of oxygen atoms in P-O-P bridges between metaphosphate Q^2 and diphosphate Q^1 units (Koudelka et al., 2014). The weak band located at 480-482 cm^{-1} can be ascribed to the bending mode vibration of SO_4^{2-} (Ganguli and Rao, 1999). It was observed that a prominent and broadnening of the band at 1420-1420 cm^{-1} is due to the disorder glass structure (Muñoz-Martín,.et al, 2009). It was observed that, by increasing the $CaSO_4$, the vibration peaks slightly shifted to higer wavelength up to 35%. This shift could indicate the effect of the $CaSO_4$, thereby, influencing the shape of the network structure and create non-bridging oxygen resulting in the depolymerization of phosphate network (Hoppe, U.,et al, 2007). The summary of Raman findings and reported values are shown in Table 3**.**

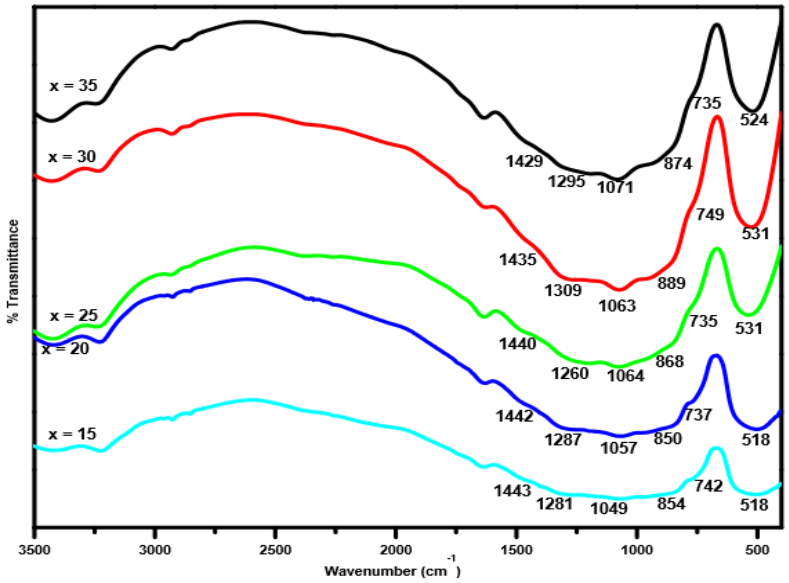


Fig.3 The IR spectra of $xCaSO_4$ - $30B_2O_3$ - (70-x) P_2O_5 with 15 ≤ x ≤ 35 mol %.

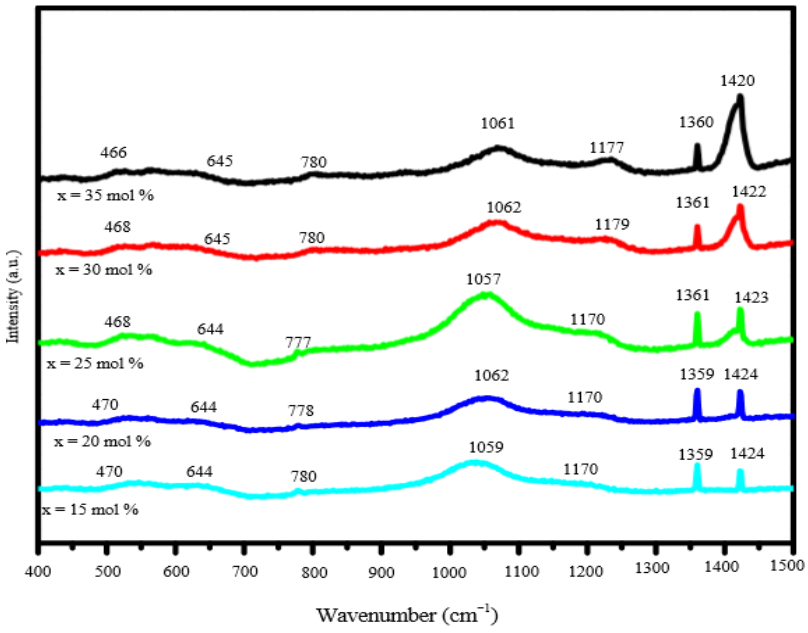


Fig.4 The Raman spectra of $xCaSO_4$ - $30B_2O_3$ - (70-x) P_2O_5 with 15 ≤ x ≤ 35 mol

Table 2 IR band assignment and the reported values for $xCaSO_4$ - $30B_2O_3$ - (70-x) P_2O_5 with 15 ≤ x ≤ 35 mol % glasses.

IR Band position in cm^{-1} with varying conc. of $CaSO_4$					Reported (cm^{-1})	Assignment
15 (mol%)	20 (mol%)	25 (mol%)	30 (mol%)	35 (mol%)		
518	518	531	531	524	500-580	Bending mode of PO_4^{3-}
742	737	735	749	735	745-760	Stretching vibration of P-O-P
854	850	868	889	874	844-964	Asymmetric vibration of P-O-P
1049	1057	1064	1063	1071	1060-1080	Mixture from $v(SO_4)$ and $v(BO_4)$
1281	1287	1260	1309	1295	1240-1350	Boroxol rings
1443	1442	1440	1435	1429	1400-1450	Stretching vibration of trigonal BO_3

Table 3 Raman band assignment and the reported values for $xCaSO_4$ - $30B_2O_3$ - (70-x) P_2O_5 with 15 ≤ x ≤ 35 mol % glasses.

Raman Band position in cm^{-1} with varying conc. of $CaSO_4$					Reported (cm^{-1})	Assignment
15 mol %	20 mol%	25 mol%	30 mol%	35 mol%		
470	470	468	468	466	465	Bending mode vibration of SO_4^{2-}
644	644	644	645	645	645	P-O-P bridges between metaphosphate Q^2 and diphosphate Q^1 units
780	778	777	780	780	720-780	Symmetric strength vibration of BO_3 and BO_4 groups
1059	1062	1057	1062	1061	1060	Symmetric stretching vibration of the tetra hedral SO_4 and BO_4 units
1170	1170	1170	1179	1170	1165-1180	Symmetric vibration of PO_2 of metaphosphate Q^2
1359	1359	1361	1361	1360	1200 -1400	Asymmetric stretching vibration of BO_3 units
1424	1424	1423	1422	1429	1420 -1485	Asymmetric stretching vibration of BO_3 units

Thermal Differential Analysis

The results of DTA measurements are shown in Fig. 5. The sharp endothermic peak is corresponding to the melting temperature (T_m) at 669-702℃, the exothermic peak is corresponding to the crystallization temperature (T_c) at 519-557℃ and the tiny peak is corresponding to the glass transition temperature (T_g) at 428-438℃. (Gilbert, J. C. & Nocedal, J. 1992) Both the glass transition temperature and the crystallization temperature increases with an increasing $CaSO_4$ content. Table 4 displays the values of T_g, T_c and T_m and calculated glass stability (S) and Hruby parameter for the borophosphate glasses. It was obseved that the thermal analysis depicts an increase of glass transition due to the addition of B_2O_3. This is an indication that combining P_2O_5 and B_2O_3 improves the strength of the host. The thermal Hruby parameters of SBP1 and SBP2 has been observed to be 0.6067 and 0.6225. This falls around the limit of thermal Hruby of 0.5 as reported by (Alajerami et.al., 2012). This shows that samples SBP1 and SBP2 could be considered as the best glass former with good thermal stability among the prepared samples.

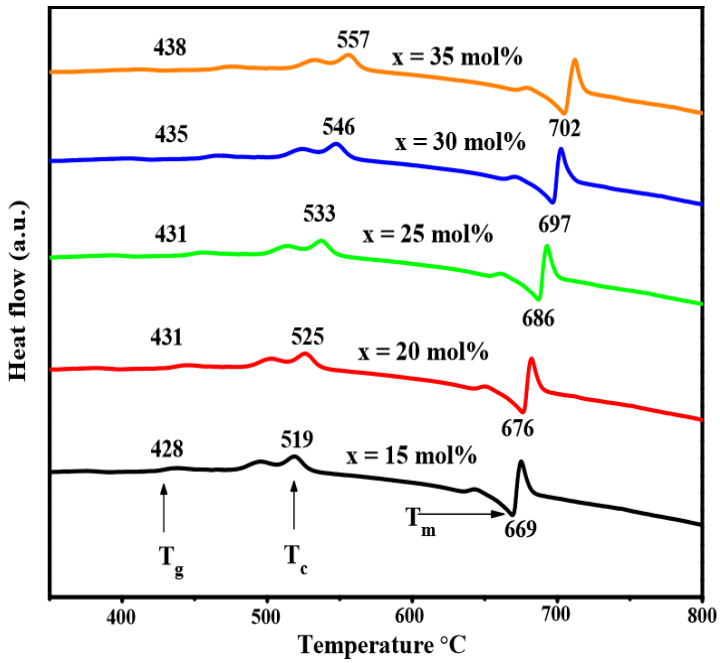


Fig. 5 The DTA spectra of $xCaSO_4$ - $30B_2O_3$ - (70-x)P_2O_5 with 15 ≤ x ≤ 35 mol %.

Table 4 $CaSO_4$ concentration dependent thermal properties of the prepared glasses.

Glass code	T_g(℃)	T_c (℃)	T_m(℃)	$S = T_c - T_g$ (℃)	H
SBP1	428	519	669	91	0.6067
SBP2	431	525	676	94	0.6225
SBP3	431	533	686	102	0.6666
SBP4	435	546	697	111	0.7350
SBP5	438	557	702	119	0.7986

CONCLUSIONS

The structural properties of sulphate borophosphate glasses containing calcium oxide were investigated in the range $xCaSO_4 - 30B_2O_3 - (70\text{-}x)\ P_2O_5$ with $15 \leq x \leq 35$ mol % composition line. The amorphous nature of the glass is comfirmed by XRD analysis. The IR spectra of these glasses show the existence of BO_3, BO_4, PO_4^{3-}, P-O-P and SO_4. The IR and Raman studies indicated that the increase of $CaSO_4$ content influence significant effect of the network structure and create non-bridging oxygen. Raman spectroscopy describe the structural formation changes of stable boron and phosphorus oxygen groups with characteristics of metaphosphate and diphosphate groups. The thermal properties of sulphate borophosphate glasses such as the transition temperature, crystallisation temperature, stability and glass forming ability are determined from DTA analysis and found to be thermally stable. The stability factor (S) is found in the range of 91 – 119 ^{0}C which indicates an increasing stability with addition of $CaSO_4$ concentration. It is found that sample SBP1 and SBP2 have good glass forming ability and stability among the prepared glass samples. Glass density and molar volume is found to be between 2.146 to 2.314 gcm^{-3} and 45.794 to 48.880 m^3mol^{-1} respectively. The obtained findings may provide some useful information towards the development of sulphate borophosphate glasses based solid state lasers.

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